Synthesis of Extended π-Polycycles Possessing Phenanthrene Unit by Oxidative Ring Expansion Reaction

博士論文

Synthesis of Extended π-Polycycles Possessing Phenanthrene Unit by Oxidative Ring Expansion Reaction

（酸化的環拡大反応を用いたフェナントレン骨格を含む拡張π多環式化合物の合成）

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令和 2 年

論文目次

Abstract

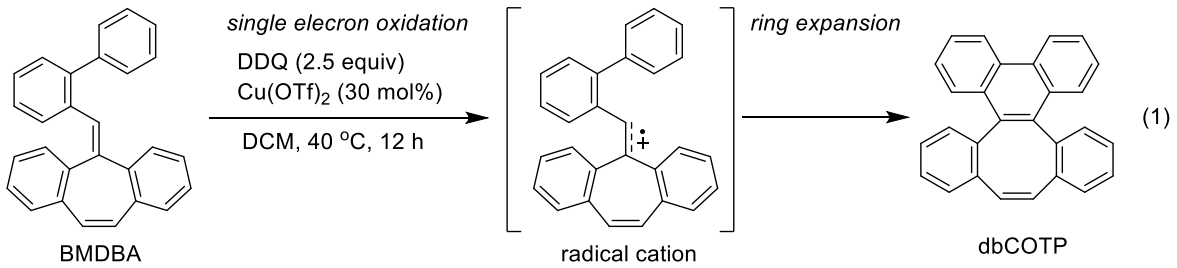
Introduction

π-Extended polycycles including polycyclic aromatic hydrocarbons (PAHs) and polycyclic heteroaromatic molecules (PHAs) have attracted significant attention for application in various organic electronics such organic field-effect transistors, organic light emitting diodes, and organic photovoltaics owing to their promising charge-carrier transporting property, light emitting performance, and narrow energy bandgap. In this context, we have recently been interested in developing new synthetic methodologies involving single electron oxidation of alkene moieties toward highly fused π-systems.[1] The present doctoral dissertation focused on developing novel synthetic methods for π-extended polycycles possessing phenanthrene unit by oxidative ring expansion reactions.

Results and discussion

1. Tandem Oxidative Ring Expansion for Synthesis of Dibenzocyclooctaphenanthrenes

Polycyclic arene units with negative curvature are prevalent in various curved nanographenes and hypothetical toroidal carbon nanotubes, which have attracted increasing attention in the field of theoretical chemistry, synthetic chemistry as well as materials science in terms of their negatively curved structural features and electronic properties. Embedding eight-membered carbon rings into the PAH frameworks has been regarded as an intriguing strategy for the construction of the negatively curved polycyclic arenes. Recently, we have developed a novel and general synthetic method for constructing a new class of polycyclic arenes embedded with a cyclooctatetraene (COT) ring by the tandem oxidative ring expansion (eq. 1).[2] The *o*-biphenyl-tethered methylene dibenzo[7]annulenes (BMDBA) could be oxidized by the DDQ/$Cu(OTf)_2$ system efficiently to the corresponding saddle-shaped dibenzo-[3,4:7,8]cycloocta[1,2-*l*]phenanthrenes (dbCOTPs) fused with an eight membered ring and a phenanthrene moiety through the formation of radical cation followed by ring expansion reaction. The present protocol provides a new synthetic approach to polycyclic arenes containing eight-membered ring, which is expected to be highly applicable for the synthesis of diverse negatively curved nanocarbons.



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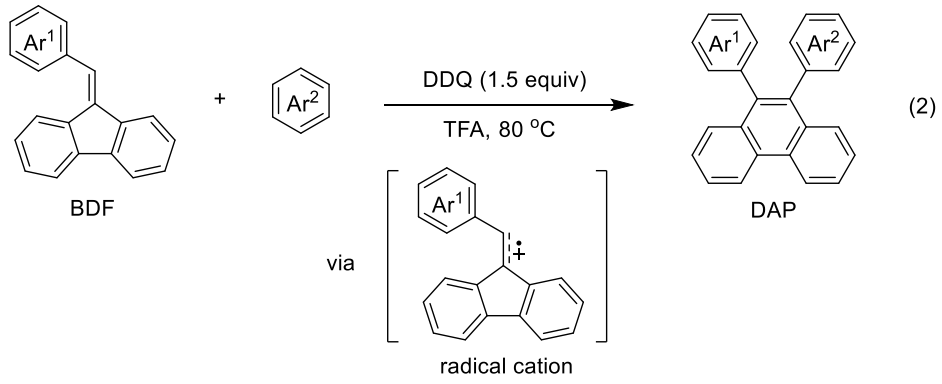
2. Synthesis of 9, 10-Diarylphenanthrenes by Intermolecular C-C Coupling and Oxidative Ring Expansion Sequence

The extended PAHs have received significant interdisciplinary attention due to their semiconducting applications in diverse organic electronics as well as intriguing structural interests of well-defined graphene segments. Phenanthrene skeletons are often incorporated in various organic functional

materials such as organic light-emitting diodes and photoluminescence materials. Therefore, many efforts have been done for developing new and efficient synthetic methods. Among them, transition-metal-catalyzed reactions realized the phenanthrene synthesis under milder reaction conditions. For example, cycloisomerization of *o*-alkynylbiphenyls, olefin metathesis of 2,2'-divinylbiphenyls, intermolecular annulation of biphenyl with alkynes were well-established for the efficient synthesis of phenanthrenes. However, these methods suffered from drawbacks, such as poor functional group tolerance and tedious substrates preparation. Recently, we developed a highly efficient intermolecular C-C coupling/oxidative ring expansion sequence for the construction of extended PAHs possessing phenanthrene unit (eq. 2). The DDQ/TFA oxidation system enables the single electron oxidation to take place preferentially at the more electron-rich alkene moiety of 9-benzylidene-9*H*-fluorene (BDF), giving rise to the subsequent tandem ring expansion process. A variety of extended PAHs involving functionalized DAPs have been synthesized in good to high yields without pre-functionalization of aromatic rings. It is worthy to mention that a broad functional group were tolerated, especially the bromo- or dibromo- substituted thiophens, which are usually not compatible under metal-catalyzed conditions. Furthermore, the Friedel-Crafts/oxidative ring expansion/dehydrogenative cyclization reaction sequence could be realized in one-pot to give the distorted dibenzo[*g*,*p*]chrysenes (DBCs). The present tandem reaction was successfully applied to a twofold coupling-annulation sequence, affording the thiophene-tethered phenanthrene co-oligomers.



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